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BP301T — Pharmaceutical Organic Chemistry II

B.Pharm Semester 3

3 hrs/week · 4 credits · 45 hours · 100 marks (25 internal + 75 end-semester, 3 hr paper)

Complete notes — all 5 units in one PDF

- Unit 1 — Benzene and its derivatives
- Unit 2 — Phenols, aromatic amines and aromatic acids
- Unit 3 — Fats and oils
- Unit 4 — Polynuclear hydrocarbons
- Unit 5 — Cycloalkanes

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BP301T — Pharmaceutical Organic Chemistry II

B.Pharm Semester 3 · Unit 1 — Benzene and its derivatives

Unit I: Benzene and its derivatives

Aromatic character

Benzene is a planar cyclic system with six delocalised pi electrons. Aromaticity requires a cyclic, approximately planar, continuously conjugated system with 4n + 2 pi electrons. This rule is a useful model, but its application to unusual systems should be checked against the prescribed text.

Evidence for the structure of benzene came from its formula, substitution pattern, equal carbon-carbon bond lengths and characteristic reactions. Resonance descriptions represent electron delocalisation, not rapidly switching structures. The orbital model describes overlap of p orbitals above and below the ring.

Electrophilic aromatic substitution

In nitration, an electrophile is generated in a strongly acidic medium and the aromatic ring forms a sigma complex before losing a proton. Sulphonation is reversible under suitable conditions. Halogenation requires activation of the halogen by a Lewis acid. Friedel-Crafts alkylation forms a carbon-carbon bond but can suffer from rearrangement and polyalkylation. Friedel-Crafts acylation forms an acylated aromatic compound and usually avoids carbocation rearrangement.

Orientation and reactivity

An existing substituent changes both the rate and position of a second substitution. Electron-donating groups generally activate the ring and direct incoming electrophiles to ortho and para positions. Strong electron-withdrawing groups generally deactivate the ring and direct to the meta position. Halogens are an important exception: they deactivate the ring but direct mainly to ortho and para positions. The exact behaviour of a substituted system should be checked against the prescribed text when more than one group is present.

Named compounds in the syllabus

The syllabus includes DDT, saccharin, BHC and chloramine. Study their verified names, functional groups, preparation or manufacture where prescribed, properties, hazards and approved uses from a current monograph. Compound-specific uses and safety classifications

should be taken from a current monograph.

Unit I: Frequently asked questions

Q: Why does benzene usually undergo substitution rather than addition?

A: Substitution can restore aromaticity after the electrophile is introduced, whereas addition would permanently reduce aromatic stabilisation.

Q: What is the sigma complex?

A: It is the temporary cationic intermediate formed when an electrophile bonds to the aromatic ring before proton loss restores aromaticity.

Q: Why are halogens unusual directing groups?

A: Halogens withdraw inductively and deactivate the ring, but their lone-pair donation stabilises ortho and para sigma-complex forms relative to meta forms.

Unit I: Key takeaways

- Aromaticity depends on cyclic conjugation, approximate planarity and the 4n + 2 rule.
- Electrophilic aromatic substitution proceeds through a sigma complex.
- Substituents affect both ring reactivity and orientation.
- Halogens deactivate but are mainly ortho and para directing.
- Compound-specific claims require verified monographs.

Unit I: Practical correlation

Practical correlation: reaction planning. A substitution experiment requires controlled reagent addition, temperature, ventilation and work-up. The exact hazard controls for a named reagent are set out in the laboratory manual.

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BP301T — Pharmaceutical Organic Chemistry II

B.Pharm Semester 3 · Unit 2 — Phenols, aromatic amines and aromatic acids

Unit II: Phenols, aromatic amines and aromatic acids

Phenols

Phenols have a hydroxyl group directly attached to an aromatic ring. They are more acidic than ordinary alcohols because the phenoxide ion is stabilised by resonance. Electron-withdrawing substituents tend to increase acidity, while electron-donating substituents tend to decrease it. Phenols undergo electrophilic substitution readily and can form ethers and esters.

Qualitative tests may use colour formation or reactions of the hydroxyl group. The reagent, expected observation and limitation of each test are set out in the current practical manual. The syllabus examples include phenol, cresols, resorcinol and naphthols. Their uses and hazards must be confirmed from authoritative sources.

Aromatic amines and diazonium salts

Aromatic amines contain nitrogen attached directly or indirectly to an aromatic system. Lone-pair delocalisation can lower the basicity of an aryl amine compared with an aliphatic amine. Substituents change basicity through inductive and resonance effects.

Primary aromatic amines can form diazonium salts under cold acidic conditions. Diazonium groups can be replaced by selected atoms or groups, and can couple with activated aromatic compounds to form azo compounds. Temperature control is important because many diazonium salts are unstable. Exact reaction scope should be checked against the prescribed text for each substrate.

Aromatic acids

Benzoic acid is an aromatic carboxylic acid. Its acidity reflects stabilisation of the carboxylate ion. Electron-withdrawing groups generally increase acidity, and electron-donating groups generally reduce it. Important reactions include salt formation, esterification, decarboxylation under suitable conditions and electrophilic substitution on the ring.

Unit II: Frequently asked questions

Q: Why are phenols more acidic than alcohols?

A: Phenoxide ion is resonance-stabilised, whereas an alkoxide ion lacks the same delocalisation.

Q: What is diazotisation?

A: Diazotisation is conversion of a primary aromatic amine into a diazonium salt under cold acidic conditions with a nitrosating system.

Q: How do substituents affect benzoic acid acidity?

A: Electron-withdrawing groups usually stabilise the carboxylate ion and increase acidity, while electron-donating groups usually have the opposite effect.

Unit II: Key takeaways

- Phenol acidity is linked to phenoxide resonance stabilisation.
- Aromatic amine basicity changes with resonance, induction and substitution.
- Diazonium salts are useful intermediates but require careful temperature control.
- Benzoic acid acidity depends on substituent effects and carboxylate stability.
- Named-compound uses and tests require verified references.

Unit II: Practical correlation

Practical correlation: qualitative identification. An identification scheme should combine solubility, acid-base behaviour and a confirmatory reaction rather than rely on one colour test. The exact scheme for a named compound is set out in the current practical manual.

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B.Pharm Semester 3 · Unit 3 — Fats and oils

Unit III: Fats and oils

Composition and classification

Fats and oils are mixtures rich in triacylglycerols, which are esters of glycerol and fatty acids. Fats are usually more solid at room temperature, while oils are usually more liquid because of composition and unsaturation. Natural samples may also contain sterols, pigments, phospholipids, moisture and minor unsaponifiable matter.

Fatty acids may be saturated or unsaturated. Double-bond geometry and chain length affect melting behaviour. Cis unsaturation introduces a bend that can reduce close packing. The exact composition of a natural oil varies with source, processing and storage, and should be checked against its monograph for any named sample.

Reactions of fats and oils

Hydrolysis breaks ester bonds and produces glycerol and fatty acids. Alkaline hydrolysis is saponification and forms soap salts. Hydrogenation reduces selected carbon-carbon double bonds. Halogen addition can be used analytically to estimate unsaturation. Oxidation of unsaturated chains can produce peroxides and later aldehydes, ketones and acids, causing rancid odours and flavour changes.

Analytical constants

Common constants include acid value, saponification value, ester value, iodine value, hydroxyl value, acetyl value and peroxide value. Acid value estimates free fatty acids. Saponification value relates to the alkali required to hydrolyse esters. Iodine value estimates unsaturation. Peroxide value measures early oxidation products. Definitions, calculations and official limits are set out in the current pharmacopoeial method.

Unit III: Frequently asked questions

Q: What is saponification?

A: Saponification is alkaline hydrolysis of an ester, producing an alcohol and a carboxylate salt.

Q: What does iodine value indicate?

A: It gives an estimate of the degree of unsaturation in a fat or oil.

Q: Why do oils become rancid?

A: Oxidation or hydrolysis can produce smaller volatile or irritating compounds, especially during exposure to oxygen, heat, light or moisture.

Unit III: Key takeaways

- Triacylglycerols are major constituents of fats and oils.
- Saturation, chain length and double-bond geometry influence physical state.
- Saponification is alkaline ester hydrolysis.
- Iodine value reflects unsaturation and peroxide value reflects early oxidation.
- Analytical limits must be taken from the applicable official method.

Unit III: Practical correlation

Practical correlation: storage of oils. Protection from oxygen, light, heat and moisture can slow deterioration. The appropriate container and antioxidant requirement for a specific product are set out in its monograph.

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B.Pharm Semester 3 · Unit 4 — Polynuclear hydrocarbons

Unit IV: Polynuclear hydrocarbons

Types and aromatic systems

Polynuclear hydrocarbons contain two or more ring systems. Fused systems share atoms between rings, while linked systems are connected by a bond. Their reactivity depends on resonance distribution, steric effects and the position of substitution. Aromaticity and electrophilic substitution principles continue to apply, but the most reactive position can differ between systems.

Reactions and medicinal relevance

Polynuclear systems can undergo electrophilic substitution, oxidation, reduction and side-chain reactions depending on structure. Some members or metabolites can interact with biological macromolecules and may be toxic or carcinogenic. Do not infer safety or therapeutic use from aromaticity. Compound-specific structures, metabolites and regulatory classifications should be taken from a current monograph.

Unit IV: Frequently asked questions

Q: What is a fused polynuclear system?

A: It is a ring system in which adjacent rings share two or more atoms and the bond joining those atoms.

Q: Why can different positions in a polynuclear system show different reactivity?

A: Resonance distributes electron density unevenly, and the intermediate formed at each position has different stability.

Q: Why must safety claims about polynuclear hydrocarbons be checked separately?

A: Biological activity and toxicity depend on the precise compound, metabolism, dose and exposure route.

Unit IV: Key takeaways

- Polynuclear hydrocarbons may be fused or linked.

- Resonance distribution controls many substitution patterns.
- A named compound needs its own verified safety and use information.
- Aromaticity alone does not predict therapeutic value or toxicity.
- Avoid drawing or reproducing chemical structures in these notes.

Unit IV: Practical correlation

Practical correlation: impurity control. Aromatic starting materials and reaction intermediates should be identified with validated methods and handled according to their hazard information. The required limits for a named impurity are set out in the current pharmacopoeia.

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B.Pharm Semester 3 · Unit 5 — Cycloalkanes

Unit V: Cycloalkanes

Ring strain and conformations

Cycloalkanes are saturated cyclic hydrocarbons. Ring stability depends on angle strain, torsional strain and non-bonded interactions. Small rings have significant angle strain. Larger rings can adopt non-planar conformations that reduce strain. Cyclohexane is commonly discussed through chair, boat and related conformations, with the chair form generally preferred because it reduces several interactions.

Substitution and stability

In a substituted cycloalkane, axial and equatorial positions are not equivalent. Bulky substituents generally prefer equatorial positions because this reduces close interactions. A ring flip changes axial positions to equatorial positions and vice versa without breaking carbon-carbon bonds. The preferred conformer is determined by the relative steric cost of substituents.

Unit V: Frequently asked questions

Q: What is ring strain?

A: Ring strain is the excess energy caused by bond-angle distortion, eclipsing interactions or non-bonded crowding in a cyclic molecule.

Q: Why is a chair conformation important for cyclohexane?

A: It gives favourable bond angles and staggered bonds, reducing angle and torsional strain.

Q: Why do bulky substituents prefer equatorial positions?

A: The equatorial position reduces close interactions with axial hydrogens and other groups.

Unit V: Key takeaways

- Cycloalkane stability depends on strain and conformation.
- Ring flips change axial and equatorial positions but not connectivity.
- Bulky substituents usually prefer equatorial positions.

- Conformation helps explain stability and reactivity.
- Chemical structures are omitted for verified preparation by Moose.

Unit V: Practical correlation

Practical correlation: conformational analysis. Comparing conformers can help explain physical properties and reaction accessibility. Any compound-specific conformational assignment should be checked against the prescribed text before use.